Symmetry, Levitation Effect and Size Dependent Diffusivity Maximum

Manju Sharma[1]**, S. Yashonath**[1]

[1] *Solid Sate and Structural Chemistry Unit*
Indian Institute of Science, Bangalore, India - 560 012

Abstract

Diffusion invariably involves motion within a medium. An universal behavior observed is that self diffusivity exhibits a maximum as a function of the size of the diffusant when the diffusant is confined to a medium, as a result of what is known as the Levitation Effect. Such a maximum in self diffusivity has been seen in widely differing medium : microporous solids, dense liquids and close-packed solids, ions in polar solvents, etc. The effect arises because the forces exerted on the diffusant by the medium in which it is confined is a minimum for the size of the diffusant for which self diffusivity is a maximum. We report here simulations on a diatomic species confined to the cages of zeolite Y. Several different simulations in which the two atoms of the model diatomic species interact with equal strength(example, O_2, the symmetric case) and with unequal interaction strengths (example, CO, asymmetric case) are modeled here. Further, the bond length of the diatomic species is varied. Our results for the symmetric case shows that self diffusivity is maximum for a large enough bond length which fits snugly into the 12-ring window of zeolite Y. For weakly asymmetric case, a weak maximum is seen as a function of the bond length of the diatomic species. However, for strongly asymmetric case, no maximum in self diffusivity is seen for all the bond lengths studied. This demonstrates close relation between symmetry and the diffusivity maximum and provides a direct evidence for the need of force cancellation to observe the Levitation Effect.

1   Introduction

Size dependence of self diffusion has attracted considerable attention over more than a hundred years.[1,2] Experimental ionic conductivities in solution with water, acetonitrile and other solvents show an anomalous dependence on ionic radii with Cs^+ having higher conductivity than Li^+ in most solvents. Early theories by Max Born[2] were followed by continuum-based theories by Hubbard and Onsager[8] and Zwanzig[15,16] and more recently, microscopic theories.[1,3,4,11,13] Very recently, work from this laboratory suggested Levitation Effect as a possible reason for the higher conductivity of the larger ions.[6] The Levitation Effect refers to the anomalous maximum in self diffusivity on the size of the
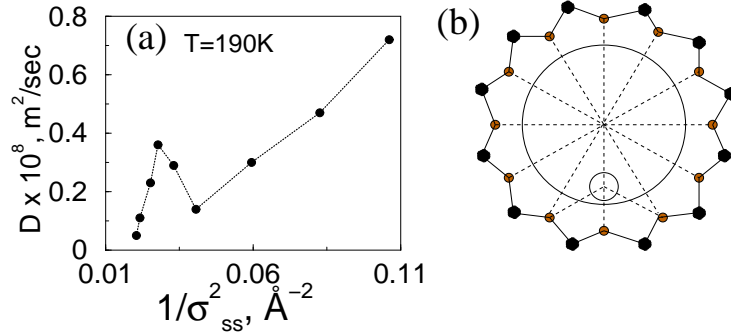
Figure 1: (a) Variation of self diffusivity as a function of the diameter of a spherical sorbate in zeolite-Y at 190K.[14] (b) Schematic representation of force acting when sorbate is small relative to the bottleneck and when it is comparable to the bottleneck. In the latter case, the force from diagonally opposite directions are equal and opposite leading to negligible net force on the sorbate.

diffusant when the diffusant has a diameter that is comparable to the narrowest part of the void space through which it has to pass through during diffusion. Typical variation of self diffusivity with the size of the diffusant is shown in Figure 1(a). The effect of forces due to the host medium on the different sizes guests diffusing through the narrowest region host is shown in Figure 1(b). The diffusivity maximum is a generic feature that is ubiquitous and has been seen in a wide variety of phases : porous crystalline solids, dense amorphous solids, dense liquids, ions in water and other solvents.

In spite of many investigations into Levitation Effect, more detailed understanding is still lacking into the origin of this effect.

The diffusivity of diffusant decreases with increase in size as predicted by kinetic theory and Stokes-Einstein relationship. In Figure 1 very small sorbate sizes show such decrease in diffusivity with size and diffusivity is inversely proportional to the square of the size. This regime is termed as linear regime(LR). But when the size of diffusing species is similar to the narrowest region of the void(window in microporous solids, neck in phases with nanosized voids in condensed media) present in the host system through which it is diffusing, it shows enhanced diffusivity or Levitation effect. In Figure 1 the sorbates which show increase in diffusivity with increase in size belong to anomalous regime(AR) and in

this regime the sorbate with size similar to the window or neck region shows diffusivity maximum. To quantify the Levitation effect observed in different systems, a parameter called *levitation parameter*, γ is defined and it is the ratio of the optimum size of the diffusant and the narrowest region of the void in the medium.

$$\gamma = \frac{2 \times 2^{\frac{1}{6}} \sigma_{opt}}{\sigma_w} \tag{1}$$

Optimum size is when the size of diffusant is similar to the window region and thus, diffusant-host interactions are optimum, $\gamma \equiv 1$ and the diffusant hows anomalous diffusion or Levitation Effect. In case of disordered solids $\gamma < 1$. When the size of diffusant is very small than the window of zeolite, it feels net attraction towards one part of the window as can be seen in Figure 1(b) and thus perform slow diffusion. When an optimum size diffusant passes through the window of the host medium, the net forces acting on it due to the host atoms cancel out due to the similar size of diffusant and window and it acts like a weakly bound particles with a high diffusivity.

In this work, we report a molecular dynamics simulation of a diatomic model guest AB sorbed within zeolite NaY. We investigate the effect of bond length, d, of A-B on self diffusivity D of the diatomic molecule. All the results are reported in terms of a parameter, l which is half of the guest bond length, d. We find the expected anomalous maximum $D(l)$ of self diffusivity on l when the bond length A-B, d is comparable to the window diameter of the 12-membered ring, the bottleneck for diffusion. Further, we report the effect of symmetry in the behavior of the curve $D(l)$. The result demonstrates the close relationship between symmetry and the Levitation Effect.

2 Methods

2.1 Model and intermolecular potential

The simulation cell consists $2\times2\times2$ unit cells of zeolite NaY. The initial configuration has three diatomic (AB) guest molecules per cage. The unit cell coordinates of zeolite Y are taken from Fitch and coworkers.[5] Interaction between the diatomic species and the zeolite are accounted for by site-site interaction between the two sites A, B and zeolite atoms Si,

O and Na. The interactions are through Lennard-Jones potential without any long-range forces. The united atom parameters of ethane given by Jorgensen have been employed in the present work with suitable modification.[9] The parameters for guest-zeolite interaction have been obtained from the Lorentz-Berthelot combination rules. The zeolite parameters have been taken from the previous work of Kiselev and coworkers.[10] The zeolites-zeolite parameters are : (σ_{OO}= 2.5447Å, ϵ_{OO}= 1.2891kJ/mol, σ_{NaNa}= 3.3694Å and ϵ_{NaNa}=0.0392kJ/mol).

We have carried out simulations with (a) $\epsilon_A = \epsilon_B$ (symmetric case or sym) (b) $\epsilon_A \neq \epsilon_B$ (intermediate asymmetry or i-asym) (c) $\epsilon_A \gg \epsilon_B$ (extreme asymmetry or e-asym). The corresponding potential parameters for A site of diatomic species with O and Na of zeolite were derived from the combination rule. The precise values of the interaction parameters employed in the present study for symmetric case are listed in Table 1. For the intermediate as well as extreme asymmetric cases, we derived the ϵ_{Ah} parameters as follows :

$$\epsilon_{xNa}^{i-asym} = \epsilon_{xNa}^{sym} \pm 0.15$$

$$\epsilon_{xO}^{i-asym} = \epsilon_{xO}^{sym} \pm 0.75$$

$$\epsilon_{xNa}^{e-asym} = \epsilon_{xNa}^{sym} \pm 0.25$$

$$\epsilon_{xO}^{e-asym} = \epsilon_{xO}^{sym} \pm 1.5 \qquad\qquad x = A, B$$

The total interaction energy is

$$U_{tot} = U_{gh} + U_{gg} \qquad\qquad (2)$$

2.2 Computational Details

All the simulation runs are made in microcanonical ensemble with DLPOLY package using Verlet leapfrog integration scheme.[12] The zeolite atoms are kept frozen during the simulation. A timestep of 1fs gives a good total energy conservation of the order of 10^{-5}. A cut off radius of 20 Å is used to calculate guest-guest and guest-host interactions. All the runs have been made at a temperature of 200K and the bond length of ethane molecule is varied in the range of 1.54 to 4.0Å in increments of 0.2Å. An equilibration run of 500ps

Table 1: Lennard-Jones interaction parameters for the symmetric guest and host.

type of interaction	σ, Å	ϵ^{sym}, kJ/mol	ϵ^{i-asym}, kJ/mol	ϵ^{e-asym}, kJ/mol
AA	3.78	0.867	0.867	0.867
AO	3.16235	1.5858	0.835805	0.0858050
ANa	3.57465	0.2766	0.126636	0.0266360
BB	3.78	0.867	0.867	0.867
BO	3.16235	1.5858	2.33580	3.08580
BNa	3.57465	0.2766	0.426636	0.526636

with a production run of 1ns has been made. The position coordinates, velocities and forces of guests are stored at an interval of 25fs.

3   Results and Discussion

The guest-guest as well as guest-zeolite radial distribution functions(rdfs) for different guest sizes, l are shown in Figure 2 and 3 for different degrees of asymmetry in interaction. The guest-zeolite rdfs have been computed between guest center of mass and the oxygens of the zeolites. We see that for $l = 0.8$Å both the rdfs exhibit structure and well defined peaks suggesting a more solid-like behaviour. In contrast, the larger sizes $l = 1.6$ and 2.0Å exhibit a more fluid-like rdf with less structure. The center of cage-center of mass radial distribution is shown in Figure 4. This gives the radial distribution of the molecular center of mass of the diatomic species within the cage. For $l = 0.8$Å we see that the molecule is close to the periphery of the cage. The molecule does not occupy the central portion of the cage at all. In contrast, the diatomic species with larger l exhibit a distribution maximum at smaller r values suggesting that they are closer to the cage center. In addition the distribution for $l = 0.8$Å is narrow as compared to $l = 1.6$ and 2.0Å suggesting possible localization. This is consistent with the solid-like rdfs we see for guest-guest and guest-zeolite rdfs. We shall see that the computed self diffusivities are consistent with this.

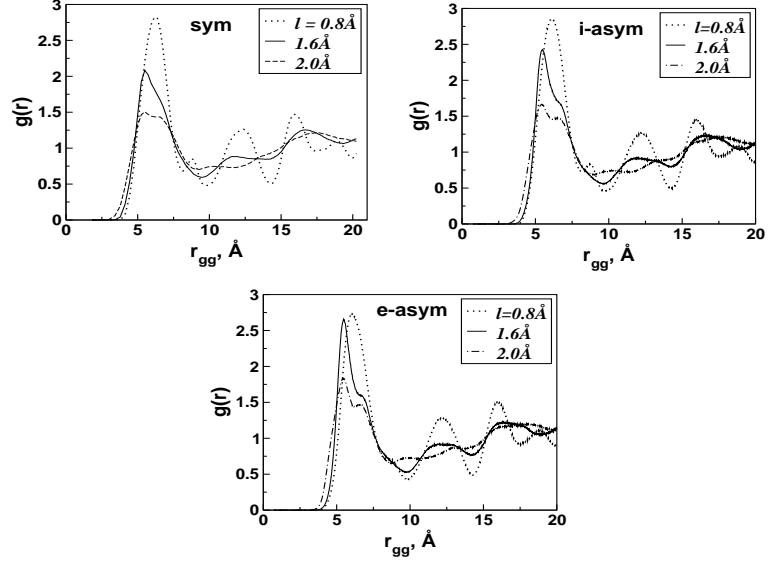The mean square displacement (MSD) for guests with different bond lengths are re-

Figure 2: Guest-guest radial distribution for a few guest sizes, l. The radial distribution function reported is between the molecular center of masses for sym, i-asym and e-asym (see text).
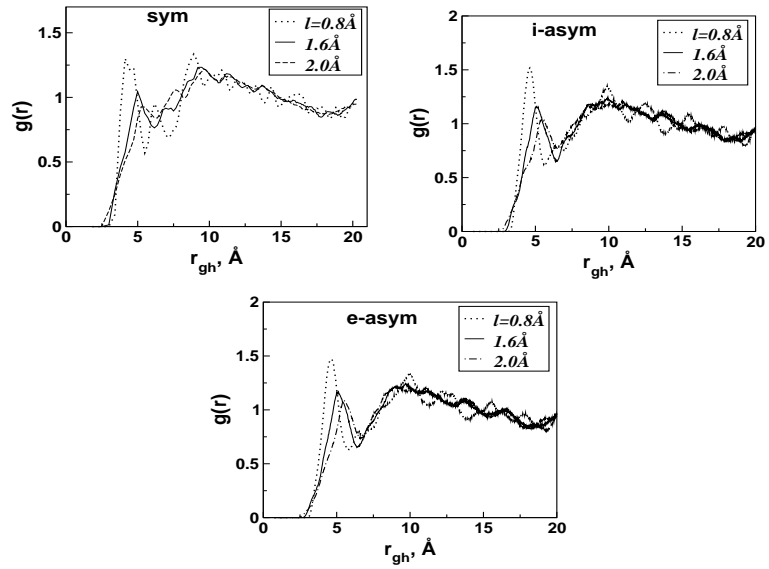

Figure 3: Center of mass of the guest-host radial distribution function, $g_{com-h}(r)$ for a few guest sizes, l, for sym, i-asym and e-asym.
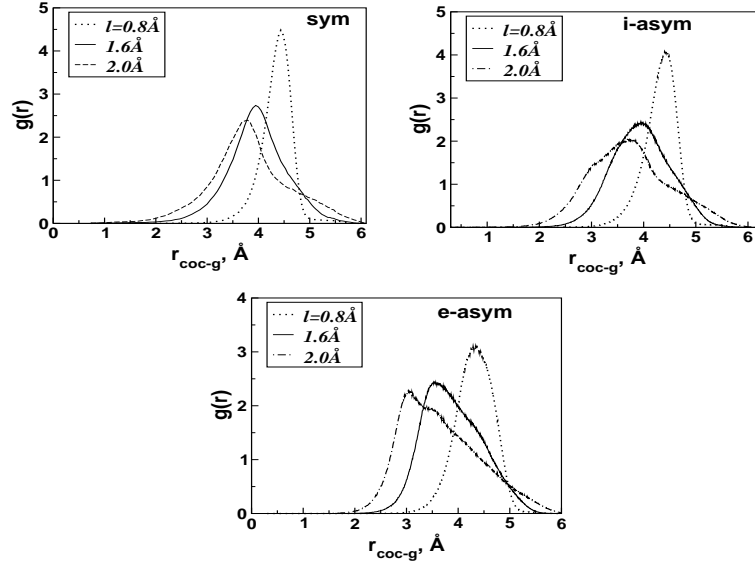
Figure 4: The center of cage to center of mass molecule radial distribution function. With increase in l, the distribution maximum shifts towards the cage center for all the three degrees of asymmetry in interaction (sym, i-asym and e-asym).

ported in Figure 5. The curves are straight which suggests good statistics. In symmetric case, there is a decrease in slope with increase in l for small guest sizes. A gradual increase in the slope of MSD is observed for intermediate guest sizes with a maximum slope for l = 1.6Å. Similar, behavior is seen for i-asym case, with maximum slope for l = 1.8Å. In case of e-asym, the slope does not exhibit an increase with increase in l and no anomalous maximum in slope is observed for any of the guest lengths. For a given guest size, l, the magnitude of the slope is least for guests of the e-asym or extreme asymmetric potential.

We show in Figure 6 the variation in self diffusivity as a function of the bond length of the diatomic molecule for the three different cases (a) sym (b) i-asym and (c) e-asym. Note the increase in D with l in the range 0.77-1.6Å for the symmetric interaction. For still larger l, self diffusivity decreases. The maximum at l = 1.6Å is seen only for the symmetric case. Another feature that is worth noting from the figure is the oscillating behavior of D with l : we see that D increases significantly on going from 0.8 to 0.9Å or 1.0 to 1.1Å or 1.2 to 1.3Å. Somewhat similar behavior has been seen in the case of window effect where the self diffusivity of various alkanes C_nH_{2n+2} as a function of n exhibit oscillatory behavior in D with n.[7]
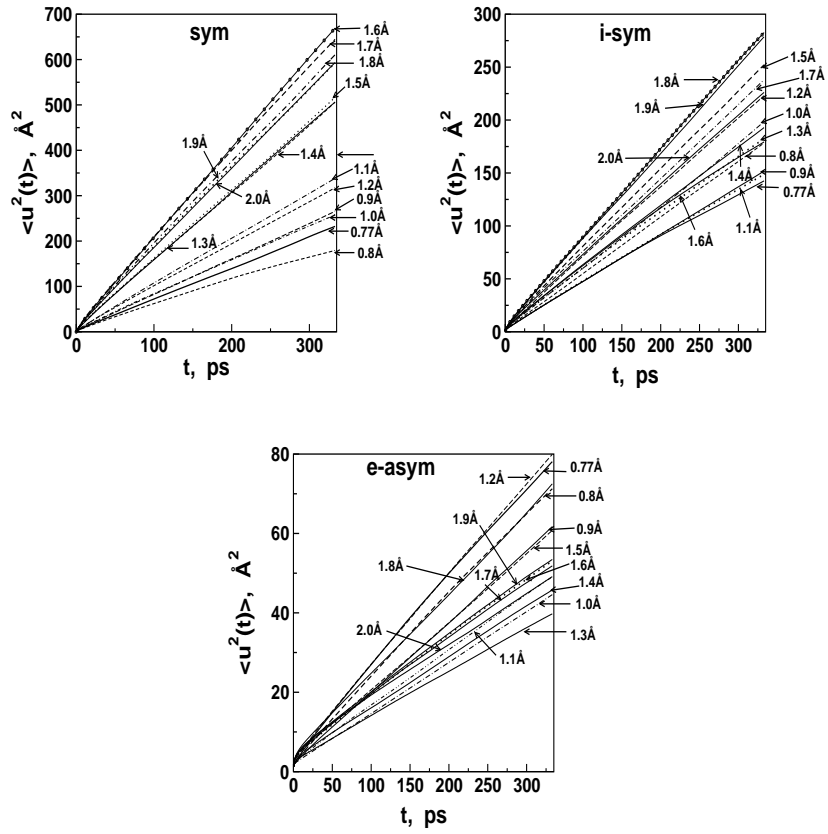
Figure 5: Time evolution of mean square displacement of guests for different values of l and the three sets involving different degrees of asymmetry in interaction : sym, i-asym and e-asym.
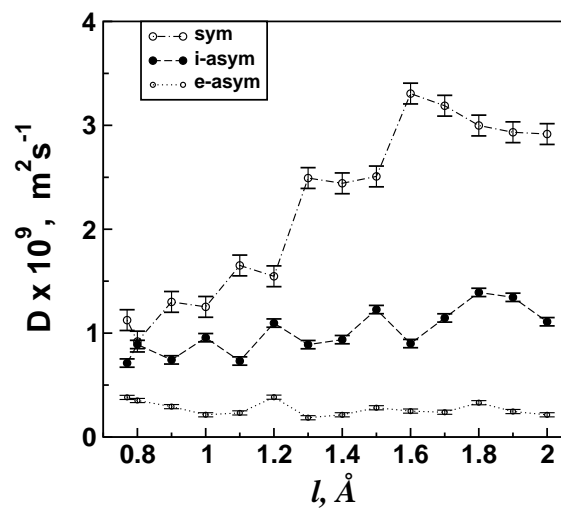
Figure 6: Diffusivity of the guest molecule as a function of the length, l in zeolite-Y at 200K in presence of different types of guest-host interaction; sym, i-asym and e-asym cases.
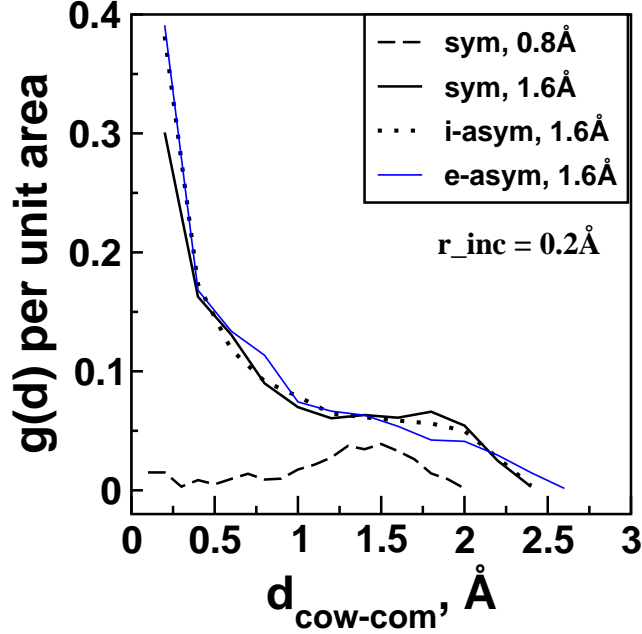
Figure 7: The distribution of center of mass of guest from the center of window when the guest is in the plane of window for guest lengths: 0.8Å and 1.6Å(sym) and 1.6Å(i-asym and e-asym).

The most important result is that as soon as asymmetry is introduced in the interactions between the guest and the host, the maximum in D vanishes almost entirely. For the large asymmetry case, there is no increase in D at all with increase in l. In fact, a slight decrease is seen upto 1.0Å before leveling off.

We note that Levitation effect has previously been noticed for monoatomic guests in zeolites, dense liquids and dense solids as well as for pentanes in zeolites. However, the present study is the first study to investigate the role of symmetry of interaction on the diffusivity maximum as a consequence of the Levitation Effect. Better understanding of the effect and the role of symmetry will provide additional insights.

Figure 7 shows a plot of distribution, f(cow-com) of the distance between the center of mass from the center of window, $d_{cow-com}$ when the diatomic molecule is in the plane of the window. When the distance between the diatomic molecule and the window plane is zero, the molecule is exiting from one of the α-cages and entering a neighbouring α-cage.

For the symmetric case, the distribution exhibits a maximum near $d_{cow-com} = 1.5$Å for the diatomic from the linear regime while the maximum in the distribution is near zero ($d_{cow-com}=0$Å) for the diatomic at the diffusivity maximum. The coincidence of the center of mass of the diatomic from anomalous regime with the window center ($d_{cow-com}=0$Å) leads to diffusivity maximum since at the window center alone there is an inversion symmetry. The presence of inversion symmetry is required for mutual cancellation of force that is responsible for the diffusivity maximum. Thus, the presence of diffusivity maximum is associated with the presence of an inversion symmetry and the passage of the diffusant through the point at which inversion symmetry exists. Here we must emphasize that the coincidence of the center of mass of the diatomic species with the window center is meant only in the statistical sense.

For i-asym as well as e-asym cases, we see that the maximum is i close to $d_{cow-com}$ = 0Å. Now, although similar coincidence with the center of window (which is also a crystallographic center of inversion) occurs, the asymmetry of interaction with the zeolite ensures that such a cancellation of forces does not occur. As a result no maximum in self diffusivity is seen when the bond length d is similar to the window diameter. The asymmetry arises because $\epsilon_{Ah} \neq \epsilon_{Bh}$ for $h = $ O, Na.

The angle between the molecular axis of the diatomic molecule and the unit vector perpendicular to the window plane when the molecular center of mass coincides with the window plane is shown in Figure 8. We see that the angle is nearly 90° and plane of the molecule coincides with the plane of the window suggesting that the molecule prefers to go with its long axis parallel to the window plane rather than perpendicular. This is because this optimizes the interaction between the diatomic molecule and the zeolite better than when the molecular axis is perpendicular to the window plane.

The activation energy barrier at the window center is a characteristic feature of the diffusant from the linear regime while the diatomic from the anomalous regime encounters either a lower barrier or even a negative barrier. Figure 9 shows the variation of the guest-zeolite interaction energy as a function of the distance from the window plane. We see that for the symmetric interaction there is significant barrier at $d_{wg} = 0$ for 1.3Å sized guest. But for the larger size of 1.6 or 1.7Å the barrier is lower. For i-asym as well as e-asym simulations, we see that the barrier is larger for 1.3 as well as 1.6Å.

The average mean square force exerted on the guest by the zeolite averaged over
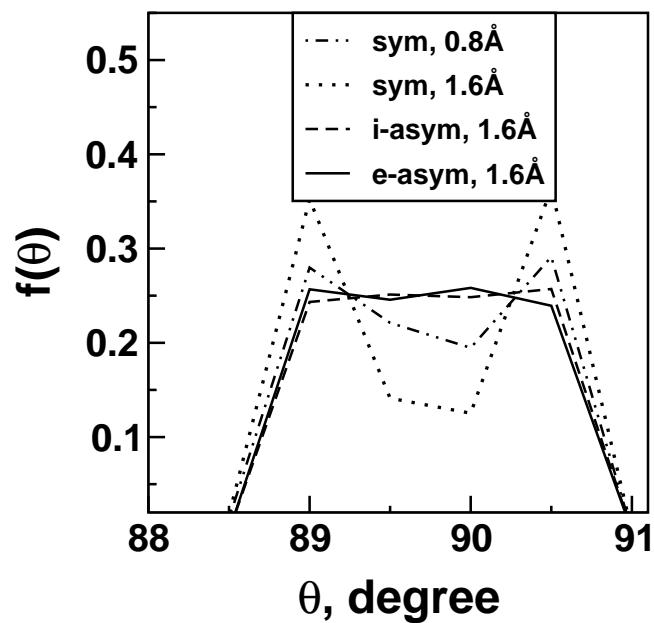
Figure 8: The distribution of angle between the unit vector perpendicular to the window plane and the molecular axis of the guest molecule: 0.8 and 1.6Å(sym), 1.6Å(i-asym and e-asym).
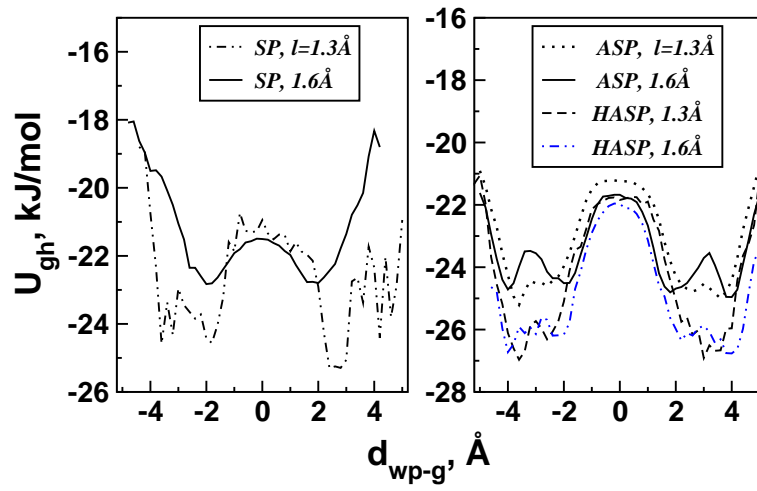
Figure 9: Variation of interaction energy of the guest with the host as a function of the distance of the guest from the window plane, $d_w p$. The energy profiles are shown for 1.3, 1.6 and 1.7Å guest lengths for symmetric case, 1.3 and 1.6Å for i-asym and e-asym cases.
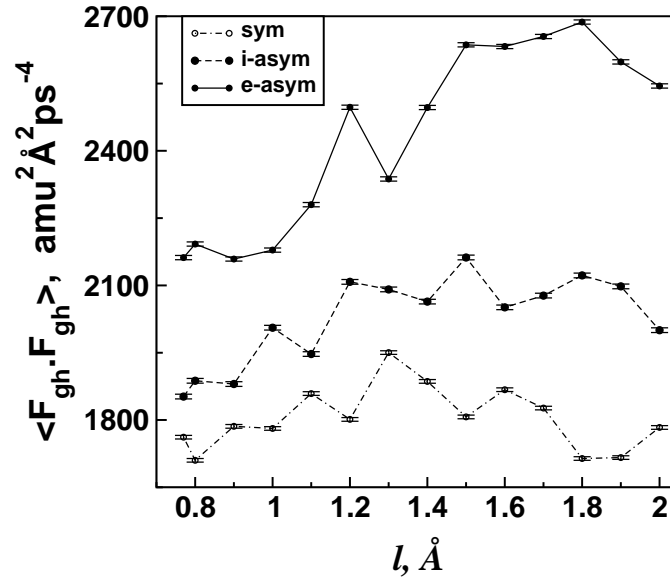
Figure 10: Average mean square force as a function of guest length, l for sym, i-asym and e-asym cases. The average mean square force is the center of mass force of the guest due to the host atoms.
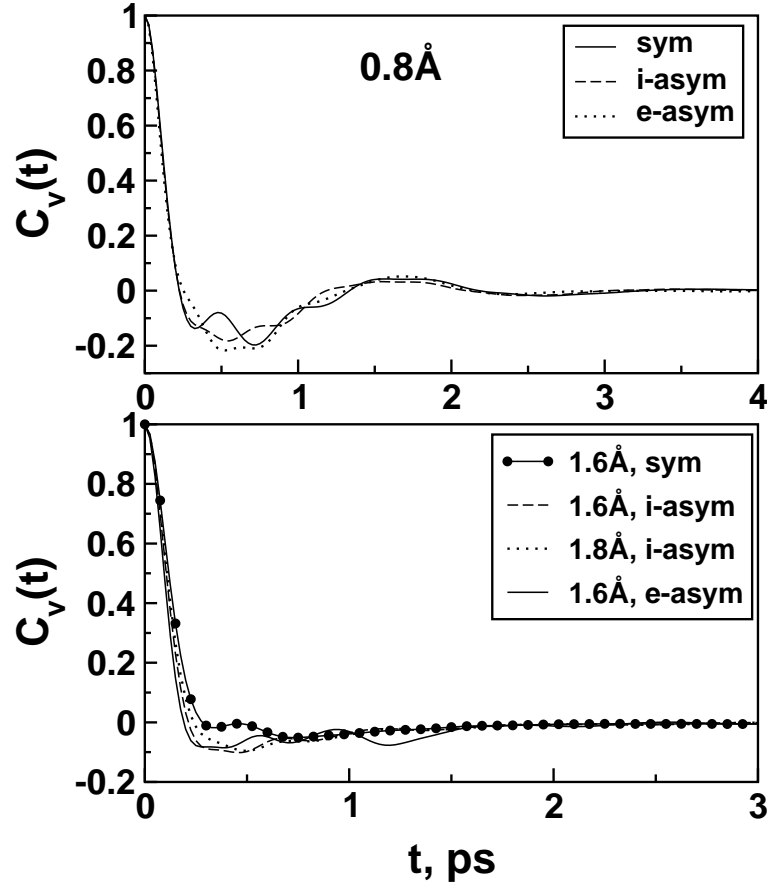
Figure 11: Velocity autocorrelation function of guests of different l diffusing in zeolite Y at 200K in presence of different guest-host interaction, sym, i-asym and e-asym cases.

all the molecular dynamics trajectory and all guests is shown in Figure 10 plotted as a function of l. We see that the average mean square force is a minimum for the l for which self diffusivity D is maximum in the case of symmetric interaction. However, with the introduction of asymmetry in the interaction, we note that the average mean square force is no more a minimum for $l = 1.6$Å. The diffusivity maximum also disappears for i-asym and e-asym sets.

The velocity autocorrelation function (VACF) for few of the guest sizes for the three different cases; sym, i-asym and e-asym are shown in Figure 11. The linear regime guest, 0.8Å shows oscillatory behavior irrespective of the nature of the interaction potential. The VACF of guest with diffusivity maximum in sym-case (1.6Å) has less backscattering as compared to the 1.6Å guest length in case of i-asym and e-asym cases and linear regime
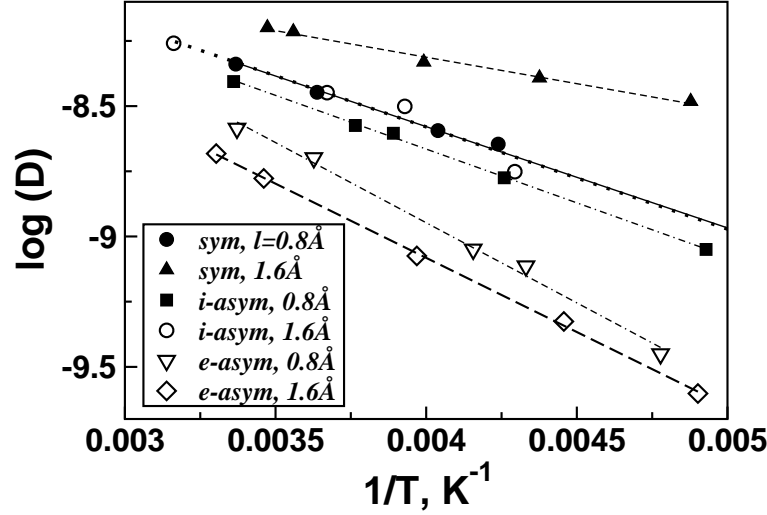
Figure 12: Arrhenius plot of the different guest lengths, l for case, sym, i-asym and e-asym obtained from the diffusivities at average temperatures (obtained from the simulation runs performed at desired temperatures of 200, 225, 250, 275 and 300K).

guest in all the cases. The guest with maximum diffusivity in case of sym-potential has a lower energy barrier at the window leading to its facile passage past the window. Linear regime guest has a higher energy barrier at the window therefore has negative correlation in the VACF. With increase in asymmetry in the guest-host potential, diffusivity maximum for intermediate guest sizes disappears which is seen with an oscillatory behavior of VACF for the intermediate guest sizes in case of i-asym and e-asym potential.

Figure 12 shows the Arrhenius plots for few of the guest sizes; sym case (0.8, 1.6Å), i-asym case (0.8, 1.6Å) and e-asym case (0.8, 1.6Å) between $ln(D)$ and inverse of average temperatures obtained from the simulation runs. The diffusivities for the Arrhenius plot have been obtained by simulating the systems at five different temperatures (200, 225, 250, 275 and 300K). The activation energies for diffusion obtained from the slope of Arrhenius plot are shown in Table 2. The activation energy is minimum for the guest length 1.6Å for symmetric interaction. This is also the guest which shows maximum diffusivity. Such a trend is not observed in i-asym and e-asym cases.

Table 2: Activation energies of guests of different l obtained from Arrhenius plot for different cases: sym, i-asym and e-asym.

case	l, Å	E_a, kJ/mol
sym	0.8	7.4358
sym	1.6	3.8927
i-asym	0.8	7.8917
i-asym	1.6	7.5054
e-asym	0.8	11.7714
e-asym	1.6	10.8939

4 Conclusions

In summary, the present work reports results for diatomic species AB in zeolite NaY. The results show that when A = B, there is a maximum in the self diffusivity of the diatomic molecule at large bond lengths d_{AB}. This suggests that Levitation Effect exists for diatomic species AA. Results when A $\neq$ B with small asymmetry in the interaction between A and B with the atoms of the zeolite shows a weak maximum in the self diffusivity. When the interaction strength between A and host atoms are made very different from that of B with host atoms, it is seen that such a maximum in D disappears completely. This suggests the absence of Levitation Effect for such a system.

A few remarks on the symmetry necessary for the diffusivity maximum or Levitation Effect is worth noting. The inversion symmetry which is essential is not the crystallographically defined symmetry which is based on structure. The necessary symmetry we require for ensuring that the Levitation Effect is seen is interaction inversion symmetry. Interaction inversion symmetry requires that the force on the diffusant from given direction is equal and opposite to the force from the diagonally opposite direction. This is less stringent a requirement than the crystallographic inversion symmetry. The latter, however, ensures the existence of interaction inversion symmetry. Situations where there is no crystallographic inversion symmetry but there is interaction inversion symmetry are when the forces arising from atoms at different distances add upto along a given direction
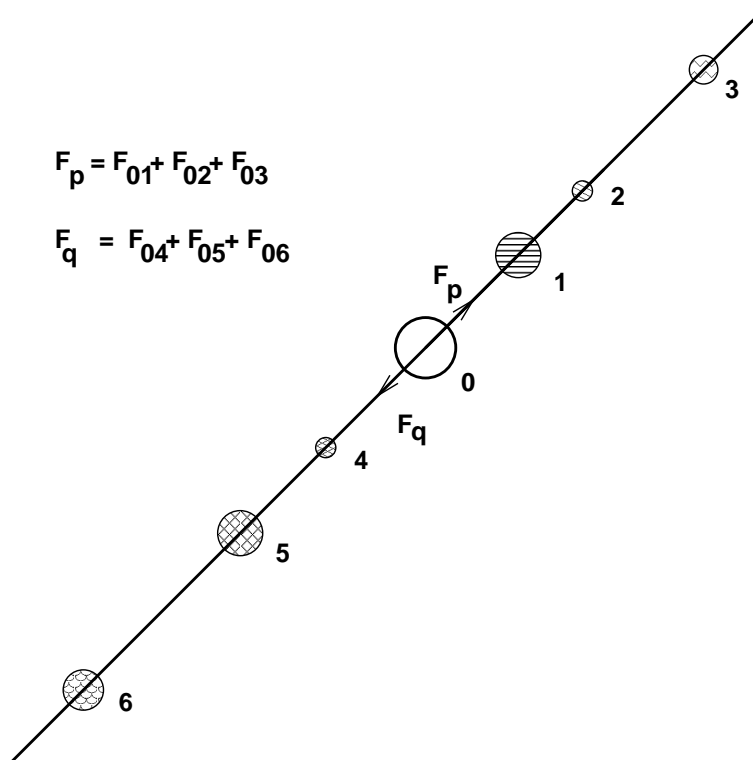
Figure 13: Schematic diagram of equal and opposite forces due to interaction inversion symmetry on center atoms occurring due to the neighboring atoms.

to say, $\mathbf{F}_p$. Now although the atomic arrangement along the diagonally opposite direction is completely different, equality should be seen along all directions.

These results suggest the role of symmetry in the interaction, leading to Levitation Effect. The present work demonstrates the need for symmetry in the interaction to observe the diffusivity maximum and Levitation Effect. Absence of symmetry in the interaction leads to obliteration of the diffusivity maximum or Levitation Effect.

References

[1] B. Bagchi and R. Biswas. *Acc. Chem. Res.*, 31:181, 1998.

[2] M. Born. *Z. Phys.*, 1:221, 1920.

[3] J. H. Chandelman and S. A. Adelman. *J. Chem. Phys.*, 72:2819, 1980.

[4] A. Chandra and S. Chowdhury. *Indian Acad. Sci.(Chem. Sci.)*, 113:591, 2001.

[5] A. N. Fitch, H. Jobic, and A. Renouprez. *J. Phys. Chem.*, 90:1311, 1986.

[6] Pradip Kr. Ghorai, S. Yashonath, and R. M. Lynden-Bell. *J. Phys. Chem. B*, 109:8120, 2005.

[7] R. L. Gorring. *J. Catal.*, 31:13, 1973.

[8] J. B. Hubbard and L. Onsanger. *J. Chem. Phys.*, 67:4850, 1977.

[9] W. L. Jorgensen, J. D. Madura, and C. J. Swenson. *J. Am. Chem. Soc.*, 106:6638, 1984.

[10] A. V. Kiselev and P. Q. Du. *J. Chem. Soc. Faraday Trans.*, 77:1, 1981.

[11] J. Rasaiah and R. M. Lynden-Bell. *Philos. Trans. R. Soc. London, Ser. A*, 359:1545, 2001.

[12] W. Smith and T.R. Forester. *The DL-POLY-2.13*. CCLRC, Daresbury Laboratory, Daresbury, UK, 2001.

[13] P. G. Wolynes. *Ann. Rev. Phys. Chem.*, 31:345, 1978.

[14] S. Yashonath and P. Santikary. *J. Phys. Chem.*, 98:6368, 1994.

[15] R. Zwanzig. *J. Chem. Phys.*, 38:1603, 1963.

[16] R. Zwanzig. *J. Chem. Phys.*, 52:3625, 1970.